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URANIUM-OXYGEN RADIATION STUDIES

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Calspan Corporation

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20. Abstract (Continued)

to the U/O₂ mixtures. Higher temperature data, however, raised questions of the attainment of full equilibrium. Thus, the results to date are limited to providing an upper bound of 500 cm⁻² atm⁻¹ to values of effective band strengths for the U/O₂ mixtures. Supporting experimental and theoretical studies are also described. Finally, recommendations for final and definitive measurements are discussed, based on improved LN₂-cooled optics and simultaneous atomic absorption spectra.

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PREFACE

This is the Final Report on Contract DNA 001-72-C-0098 and covers the period July 1972 through April 1973. This work was sponsored by the Defense Advanced Research Projects Agency and monitored by Dr. Charles A. Blank of the Defense Nuclear Agency.

Contributors to the research reported herein were Drs. C. E. Treanor, W. H. Wurster, and J. Raymonda of the Aerodynamic Research Department at Calspan.

TABLE OF CONTENTS

SECTION	PAGE
1 TECHNICAL SUMMARY	5
2 DESCRIPTION OF THE EXPERIMENTAL METHOD . .	7
2.1 GENERAL DISCUSSION	7
2.2 APPARATUS DESCRIPTION	9
3 CHARACTERIZATION OF LWIR RADIANCE FROM U/O ₂ /A MIXTURES	14
3.1 EARLY RESULTS	14
3.2 LATER RESULTS	20
4 SUPPORTING EXPERIMENTS	23
4.1 SPECIES CONCENTRATIONS	23
4.2 AEROSOL GENERATION AND SPATIAL DISTRIBUTION	28
5 SUPPORTING THEORETICAL CONSIDERATIONS . . .	31
6 CONCLUSIONS AND RECOMMENDATIONS	34
REFERENCES	38
APPENDIX I . NOTES ON URANIUM AND URANIUM OXIDE THERMO FUNCTIONS	41

LIST OF ILLUSTRATIONS

FIGURE		PAGE
1	Schematic Diagram of the Aerosol Shock Tube Experiment for Quantitative Spectral Radiance Measurements in Uranium-Oxygen Mixtures	10
2	x-t Diagram for 360 PSI HE \rightarrow 30 Torr 5% O ₂ /A	13
3	Typical Spectra from Calspan Aerosol Shock Tube	15
4	Uranium Aerosol Shock Tube Spectra	16
5	Time Dependence of 11.8-13.8 μ m Gas Radiance After Shock Reflection (R) For Three Different Test-Gas Compositions at 5200°K: (A) Argon, (B) 5% Oxygen/95% Argon, (C) Uranium Aerosol in 5% Oxygen/95% Argon	18
6	Wavelength Dependence of the Measured Emissivity for the Oxides of Uranium in 5% Oxygen/95% Argon, at T = 4500°K	19
7	Time Dependence of 10-12 μ m Gas Radiance After Shock Reflection (R) For Uranium Aerosol in 5% Oxygen/95% Argon at 5400°K	21
8	Emission Line Spectrum of Uranium Aerosol in Argon at 5700°K (Visible Spectral Region)	25
9	Schematic Diagram of the Optical Technique for Obtaining Absorption Spectra of Shock-Heated Aerosols	27
10	Typical Records of Gas Radiance Behind the Incident Shock During Passage Down the Shock Tube. The Height of the Leading Edge of the Pulse is Proportional to the Aerosol Concentration at that Station. (A) Aluminum, (B) Uranium. Sweep Rate was 500 μ s/cm	30
11	Calculated Species Concentrations for Given Conditions	32
12	Apparatus for Simultaneous Atomic Absorption and High-Sensitivity LWIR Radiance Measurement	35
13	Blackbody Radiance Curves Showing the Effect of Decreasing the Background Temperature from 350°K	36

SECTION 1

TECHNICAL SUMMARY

This report is the Final Report on a research program whose objectives are to measure absolute spectral radiances from uranium-oxygen mixtures. The measurements are made under controlled conditions of temperature and species concentrations, and include infrared data.

The initial program was undertaken to assess and demonstrate the applicability of the Calspan exploding-wire-aerosol shock tube facility toward obtaining the required data. Recently, the contract was amended to extend the period of performance to April 1973, to complete these radiation studies. This report is presented from the overall point of view of the contract as it was finally structured. As such, this technical summary very briefly reviews the overall problem, the method of attack, and the results. Details are contained in the subsequent body of this report.

The general problem of metal oxide radiation under various environmental conditions depends upon two items: the gasdynamic and thermodynamic conditions that prevail, which, coupled to the kinetics determined the various oxide concentrations and degree of excitation; secondly, given the aforementioned information, additional data are needed to specify the absorptive and radiative behavior of these oxide molecules. It is the latter question to which the present studies are addressed.

The experimental plan was to produce an aerosol of uranium in a controlled mixture of oxygen and inert gas such as argon. This aerosol is shock-heated, thereby vaporizing the metal particles, and providing a gaseous mixture of U, O₂ and argon at high, equilibrium temperatures. The final data comprise absolutely measured spectral radiances over wavelength regions of interest. The parameters of the experiment are the temperature, relative U/O₂ ratios and wavelength range and resolution. Details of the technique are given later in the report, as well as evidence for the very clean spectra that result. This is an important feature of the technique,

because quantitative radiometric measurements only have meaning if it has been separately shown that the radiating species have been identified.

The primary data comprise the infrared radiance measurements between 8 and 14 μ m. Early results indicated high values of effective band strengths from the shock-heated $U/O_2/A$ mixtures. However, subsequent tests at higher temperatures revealed nonequilibrium features in the data. Because the question of these features could not be resolved within the scope of the program, the results to date are limited to establishing an upper bound to the LWIR radiation.

Supporting measurements were conducted during the course of the program. The objectives of these studies included (a) the application of the exploding-wire aerosol shock tube technique to infrared radiance measurements of metallic oxides, (b) studies of the generation and spatial distribution of the uranium aerosols, (c) relevant species concentration measurements. These supporting studies are discussed in the report.

In addition, a supporting theoretical effort was undertaken. This effort involves the use of best available data to provide thermodynamic functions of uranium atoms and oxide molecules. These functions are used to calculate the relevant species concentrations for the thermodynamic conditions generated in the shock tube. They are especially useful in providing scaling parameter checks for proper identification of radiating species in the test gas.

SECTION 2

DESCRIPTION OF THE EXPERIMENTAL METHOD

2.1 GENERAL DISCUSSION

Several methods have been reported which address the problem of obtaining metals and metal oxides in gaseous mixtures for spectroscopic studies. They include ground metal slurries on substrates, the use of metal-organic compounds, and particulate dust injection.^{1, 2} For spectroscopic studies, it can be appreciated that the use of any substances other than the pure metal of interest results in overlapping, contaminated spectra which can seriously compromise the subsequent analyses. This is especially true for IR measurements, where the use of photographed spectra is precluded, and the identification and subtraction of radiating species in contaminated spectra is rendered prohibitively difficult.

The method developed at Calspan,^{3, 4} which is described in the following section, has been shown to produce very clean spectra. In aluminum, as will be shown later, the spectra contain only atomic Al resonance lines and the blue-green band system of AlO. No hydrocarbon species were present; the usual Na and Ca lines were the only background radiators. This work with Al was performed earlier for ARPA, and subsequent studies to complete the development of the technique were carried out under Calspan Internal Research funding. These studies have put the technique on a sound basis, and it was applied directly to the present research problem.

The overall experimental method takes advantage of the use of shock tubes to produce sources of gas at high equilibrium temperatures. Essentially, the method consists of exploding a wire of suitable material in a controlled atmosphere, thereby producing a metallic smoke, or aerosol, containing the particular species under study. The resultant aerosol is permitted to expand into the vacuum of the driven section of a shock tube, and is subsequently subjected to shock heating. The end result is the complete vaporization of the aerosol particles, and the formation of the molecular species of interest in the thermodynamic equilibrium.

A significant advantage of the aerosol shock tube technique for spectral radiance studies lies in the purity of the spectra that are obtained. This results directly from the fact that only the species of interest are used in the experiment. Methods utilizing metallic compounds in vapor form inherently involve fluorine, chlorine, or hydrocarbons. When combined with oxygen and then heated, the spectra stand a high degree of probability for contamination and a degradation of the desired data. In spectral regions where film is sensitive, such contamination can be recorded and taken into account. In the infrared, however, this is not the case, and hence a burden of proof of spectral purity is superimposed on the experiment. Examples of spectra demonstrating this point are presented later in this report.

The range of temperatures attainable in these experiments is a second significant feature of the technique, because the temperature dependence of the species concentrations and their excited state populations serve as a valuable diagnostic for identification. Beginning with an aerosol containing U, O and Ar, at very high equilibrium temperature ($\sim 6,000^\circ \text{K}$), one would expect predominantly neutral and ionized atomic species. As the temperature is decreased in similar tests using weaker shock waves, the molecular oxide concentrations would increase. Thus, the metal oxide band radiation can be expected to go through a maximum, limited on the low temperature side by the Boltzmann factor in excited state population, and on the high side by molecular dissociation.

For normal gases the concentration of radiating particles is known, and the emitted intensity per particle, or the optical transition probability, can be obtained from quantitative spectral measurements. In the extension of such studies to gases containing normally solid materials, it will be seen that emitter concentrations become a critical parameter. While the partial pressures of gases introduced into the shock tube test section can be accurately determined, there is no a priori way of assessing the quantity of metallic aerosol. Thus, the resultant molecular oxide emitter concentrations must be obtained by separate but simultaneous measurements on the same gas sample. This can, in principle, be accomplished by quantitative spectroscopic analysis on lines of the parent atom, for which the transition

probabilities are known. Thus, by knowing the temperature of the mixture and the atomic concentrations of the metal, the oxide concentration is obtained by calculation, using the equilibrium constant. Using this method, the final result for the metal oxide transition probability therefore depends on the atomic line f-numbers and the appropriate thermochemical constants for the metal-oxygen system.

In aluminum oxide studies this concentration measurement technique is quite straightforward. Published f-numbers for the resonance doublets of Al are available together with several determinations of the transition probabilities for the Al ($B^2 \Sigma - X^2 \Sigma$) bands. However, the relevant data for the $U-O_2$ system is much sparser and more poorly known. This applies both to thermochemical data, as well as the radiative behavior of the uranium oxides. Indeed, evidence for the identification and existence of UO bands in the IR is currently the subject of research by two groups of workers. The point to be made here is that the analysis of the spectroscopic data of these experiments will need to rely upon best available data, which are still in a state of flux. The question of concentration measurements is addressed further in Section 4 of this report.

2.2 APPARATUS DESCRIPTION

During the course of the program, a number of different diagnostic configurations were employed. These will be described where appropriate to specific investigations. For the final radiance measurements, the apparatus depicted in Figure 1 was used.

The shock tube in which the test gas mixture is heated to desired conditions has been described in detail in Reference 4. The test gas mixture itself is produced in an aerosol chamber, into which known concentrations of O_2 in argon are admitted. The uranium is introduced in the form of a thin strip mounted between two electrodes. This strip is subsequently exploded by a 2500 joule discharge, which produces the uranium aerosol. This mixture is then permitted to expand into the vacuum of the test section of the shock tube. The passage of the incident and reflected shock wave through this aerosol mixture completely vaporizes the aerosol, resulting

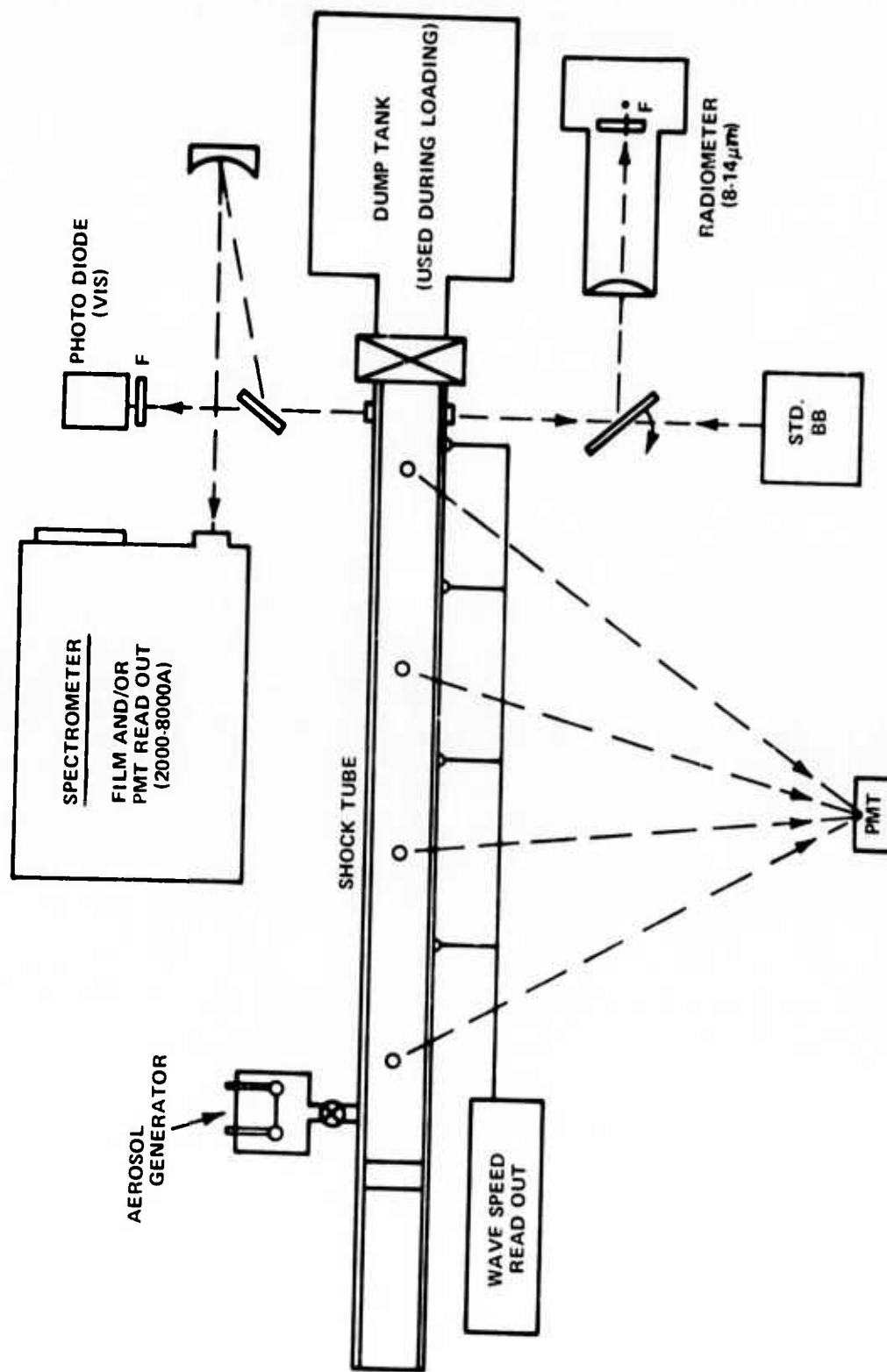


Figure 1. SCHEMATIC DIAGRAM OF THE AEROSOL SHOCK TUBE EXPERIMENT FOR QUANTITATIVE SPECTRAL RADIANCE MEASUREMENTS IN URANIUM-OXYGEN MIXTURES

in a heated gaseous mixture of uranium, oxygen, and argon at the reflecting end of the tube. This mixture is in equilibrium for some 200-300 μ seconds at temperatures that can range between 4000-8000°K, depending on the shock strength chosen for the test. The shock velocity was measured over every two-foot interval along the 12-foot test section.

The principal diagnostic instruments are located at the reflecting end of the shock tube, where the test gases are viewed through small ports with windows appropriate to the wavelengths of interest. An f/6.3 spectrometer was used to obtain spectra between 2000 and 8000°A. Used in second order, a plate factor of 10Å/mm was achieved. The instrument has optional multichannel photomultiplier readout units, which permitted selected wavelengths to be monitored temporally.

An infrared radiometer using an HgCdTe detector and germanium lens was also deployed to measure the gas spectral radiance between 8-14 μ m. Filters were used to define specific bandpasses throughout this wavelength region. The system was arranged so that a single mirror rotation permitted the radiometer to view a standard blackbody source, usually operated at 1000°K. Because the optical train was made completely identical, this procedure permitted a direct calibration of the gas radiance level to be made before and after each shock tube test.

Finally, a photodiode, filtered for the visible spectrum near 5000°A, was used to monitor overall shock tube performance; a separate photomultiplier-filter system also monitored the visible radiation emitted behind the incident shock wave as it progressed down the tube. Four window ports were used. These data provide a check on wave speed, on overall shock tube performance, and most importantly, provide a quantitative assessment of the aerosol distribution along the tube. Independent of the chemical processes that occur behind the shock wave, the instantaneous height of the leading edge of the radiation pulse is related to the aerosol concentration at that station along the shock tube. As a result of such measurements, it was found that a loading technique using a dump tank at the end of the shock tube produced a more uniform distribution than was obtained with the shock tube alone. A gate valve is used to isolate the shock tube from the dump tank during the test. This technique will be discussed further in Section 4.

The overall performance of the shock tube as it relates to heating the aerosol-test gas mixture is illustrated in Figure 2. Experimentally determined positions of the incident shock wave and the interface are used to construct the usual x-t diagram.⁵ The shock wave is observed by both heat transfer gauges and the onset of radiation at window ports. The interface, marking the arrival of the piston, or driver gas, is noted by the abrupt cessation of radiation. The onset and termination of the reflected shock test time interval (~1200-1600 sec) are, in general, readily observed by the radiation history recorded from the port at station 10.

The growth of the "test slug length" in area B can be noted. It results from the fact that the test gas moves at a lower velocity than the shock wave. Thus, the motion of elements of gas is depicted by the dotted lines. They remain at rest until shock wave arrival and are then swept down the shock tube at the gas velocity. The interaction with the reflected shock wave then ideally brings the gas to rest again, having been significantly compressed and heated. Thus, as shown, the gas ultimately situated at station 10 was originally in the central position of the tube. This point is discussed further in Section 4.

Diagrams such as those of Figure 2 served to confirm and monitor shock tube performance for the broad range of pressure and temperature conditions of interest to the present studies.

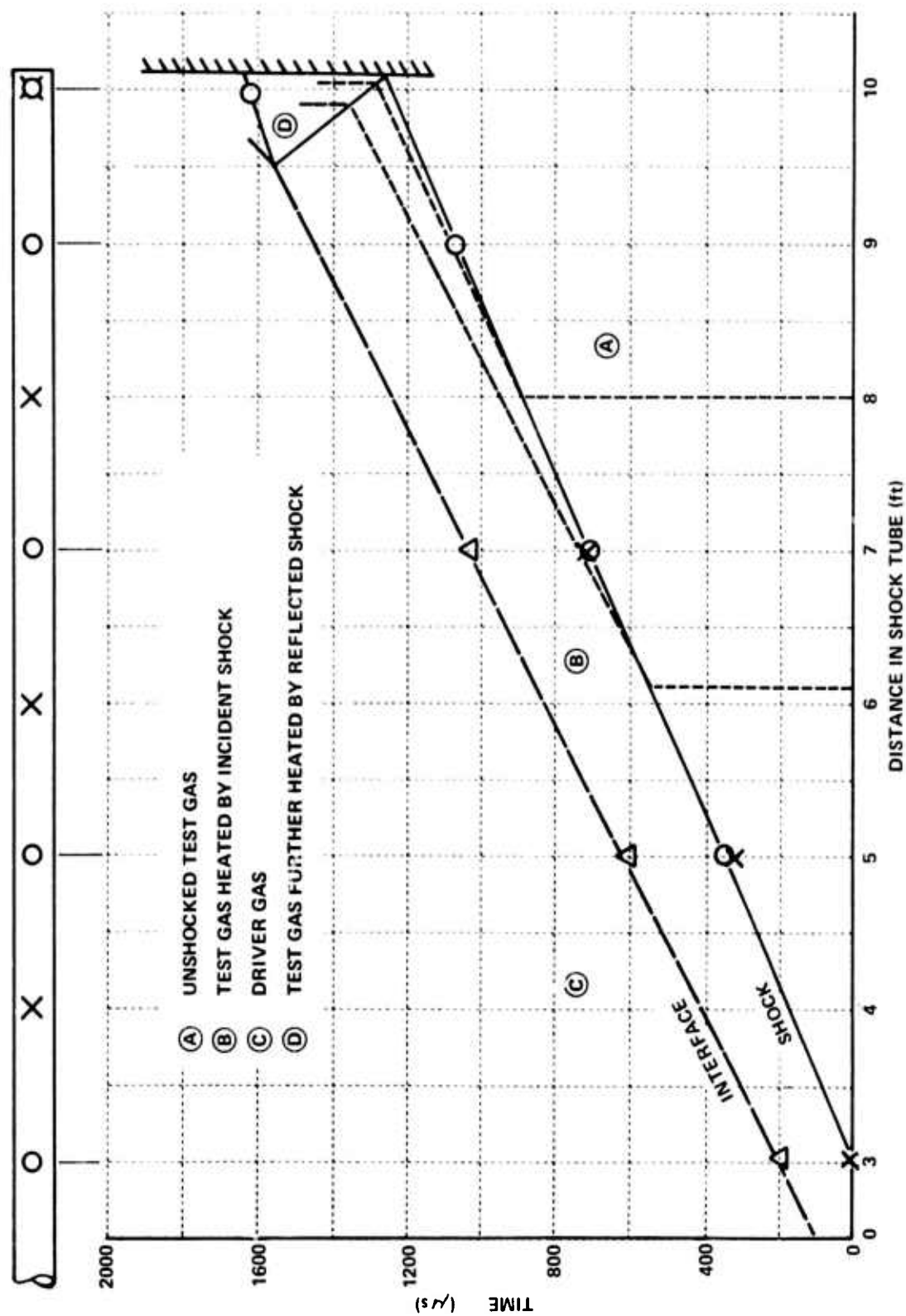


Figure 2. x-t DIAGRAM FOR 360 PSI HE → 30 TORR 5% O₂/A

SECTION 3

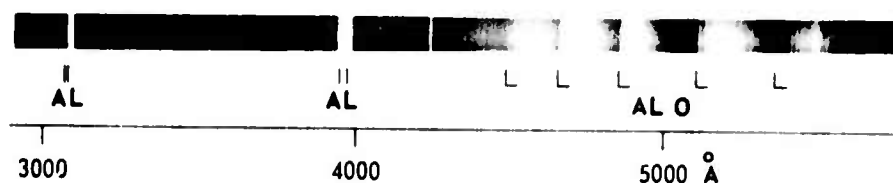
CHARACTERIZATION OF LWIR RADIANCE FROM U/O₂/A MIXTURES

3.1 EARLY RESULTS

As mentioned in the previous section, the principal advantage of the aerosol-shock tube technique for spectral radiance studies lies in the purity of the spectra that are obtained. As will be seen this advantage is of particular importance for the uranium studies. The spectra of Figure 3 are shown to exemplify this point. These spectra were taken during the course of earlier studies of the aluminum-oxygen system. With both Al and Be, the well-developed bands in the visible are clearly seen. No other molecular spectra are evident; the only atomic lines are those of the resonance doublets of Al. The only impurity lines seen are those from trace amounts of Ca and Na, which play no role in the oxide studies.

The advantage of the spectral purity discussed above can be appreciated when the spectra of uranium aerosols are studied. Some of these spectra are shown for several test conditions in Figure 4. Although the spectra were not analyzed in detail, several noteworthy features are readily discerned. In uranium-argon mixtures, the many-lined spectrum of U atoms is clearly developed. Many of these lines have been identified, and it is anticipated that these will provide a method for the quantitative assessment of the U atom concentration. Accuracy would be limited to available data on the relevant *gf* values. The influence of O₂ in the system is seen to be very marked, giving rise to an apparent continuum in this wavelength region. Equilibrium calculations (Section 5) show that under these test conditions less than 10⁻⁵ of the uranium remains as free atoms or ions, so that the line structure no longer appears.

The corresponding radiance levels in the LWIR were obtained by using the radiometer discussed in Section 2 and depicted in Figure 1. Use was made of three filters of approximately 2 μ m bandpass, to cover the region between 8 and 14 μ m. As shown in the figure, absolute calibration was achieved by a direct comparison with a blackbody standard using identical optics (an Irtran window was placed in front of the standard to compensate for the shock tube window).



AEROSOL CHAMBER -- P = 11 PSIA, 5% O₂ - 95% ARGON

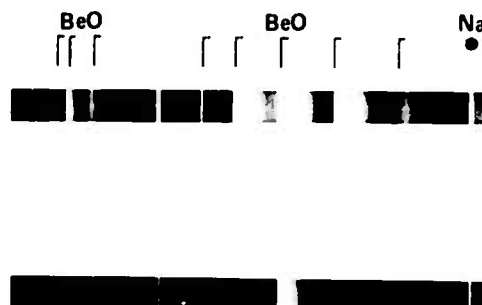
AL WIRE, 0.125 MM DIAM, 2.54 CM LENGTH

C = 1 μ F, V = 6000 VOLTS

SHOCK TUBE -- P₁ = 50 TORR, V_S = 5000 FT/SEC

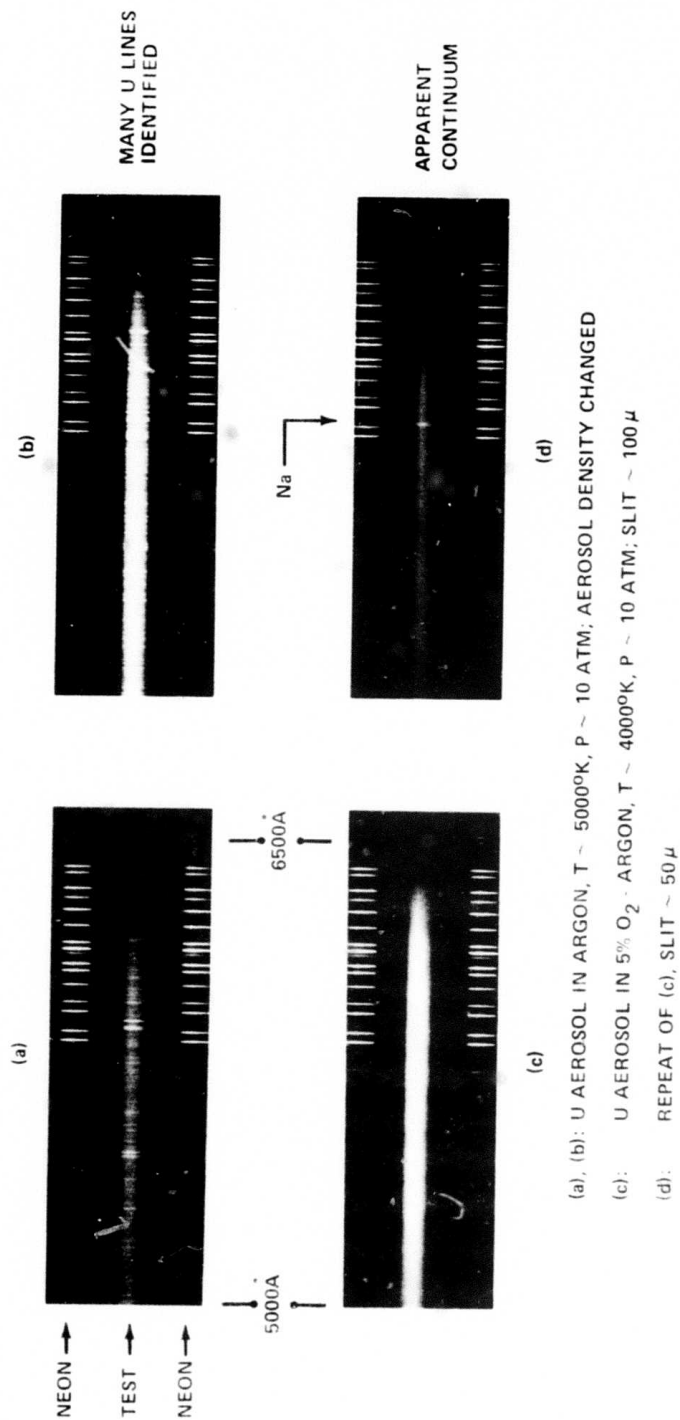
T_{REFL.} = 4000°K

ALUMINUM OXIDE SPECTRUM



BeO SPECTRA AT TWO TEMPERATURES

Figure 3. TYPICAL SPECTRA FROM CALSPAN AEROSOL SHOCK TUBE



(a), (b): U AEROSOL IN ARGON, $T \sim 5000^{\circ}\text{K}$, $P \sim 10 \text{ ATM}$, AEROSOL DENSITY CHANGED
 (c): U AEROSOL IN 5% O_2 - ARGON, $T \sim 4000^{\circ}\text{K}$, $P \sim 10 \text{ ATM}$, SLIT $\sim 100 \mu$
 (d): REPEAT OF (c), SLIT $\sim 50 \mu$

AEROSOL PRODUCED BY EXPLODING PURE U FOIL STRIP (.040 x 5/8 IN)

Figure 4. URANIUM AEROSOL SHOCK TUBE SPECTRA

Three data records showing 12-14 μm radiance as a function of time during the steady-state test interval behind the reflected shock wave (R) are shown in Figure 5. The temperature in each case was about 5200°K. Records (A) and (B) refer to tests in pure argon and 5% oxygen in argon, respectively. As is to be expected, no radiation is recorded, as oxygen is not infrared active, and the temperature is too low to excite any of the atomic levels in argon that could radiate at these wavelengths.

Adding uranium to the 5% oxygen-argon mixture gives rise to a steady level of radiance from the gas for the duration of the test time in the shock tube, as shown in Figure 5(C). It was the dependence of this radiance on wavelength, temperature and species concentration that constituted the basic objectives of the study.

The wavelength dependence of the radiance was measured by using different filters under constant test conditions, in which the uranium aerosol in 5% oxygen - 95% argon was shock-heated to 4500°K. By using the black-body calibrations, the absolute radiance was directly obtained, and the ratio of this radiance to blackbody values at the gas temperature permitted the emissivity to be calculated. Figure 6 depicts the results.

The 50% transmission points of the filters are shown. The two values at the 11.8 - 13.8 μm interval are the result of two identical tests and reflect the good experimental reproducibility. The bounded values at 10.4 - 12.4 μm represent the data spread resulting from reading the oscilloscope records. Maximum errors are estimated at 20%.

An interesting feature of these data is the relatively high emissivity values. A preliminary attempt to calculate an overall, engineering band strength was made by integrating these measured emissivity values over the 7.8 to 13.8 μm region. The amount of oxygen in the gas mixture was known, and the uranium concentration estimated from earlier measurements (in aluminum) of the aerosol yield from the exploding metal strip. As discussed in Section 5 and in Appendix I, available spectroscopic data were used to deduce the thermodynamic functions needed to calculate the concentrations of the atomic and molecular components of the gas at the measured conditions of temperature and pressure. Under these conditions

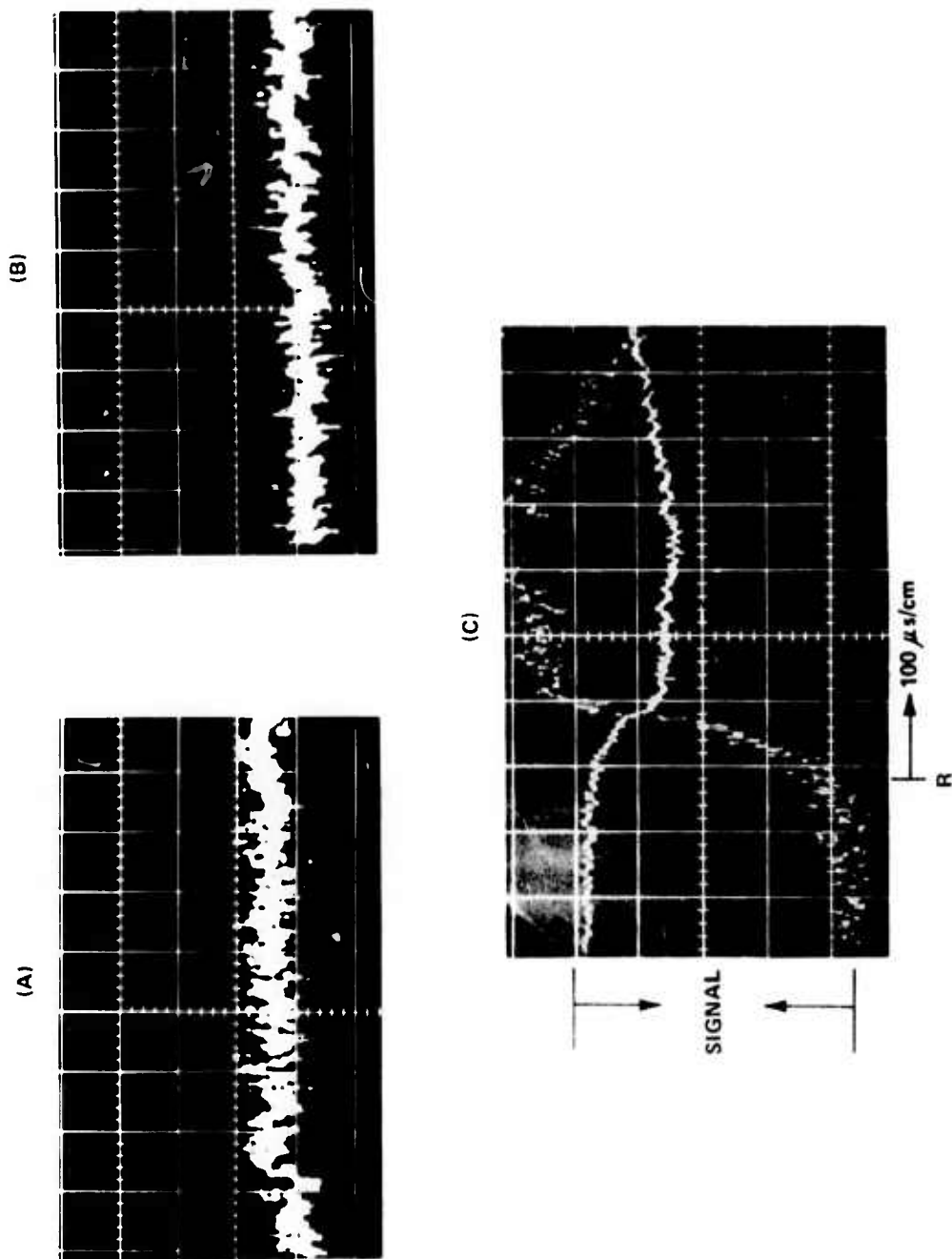


Figure 5. TIME DEPENDENCE OF 11.8-13.8 μm GAS RADIANCE AFTER SHOCK REFLECTION (R) FOR THREE DIFFERENT TEST-GAS COMPOSITIONS AT 5200°K: (A) ARGON, (B) 5% OXYGEN/95% ARGON, (C) URANIUM AEROSOL IN 5% OXYGEN/95% ARGON

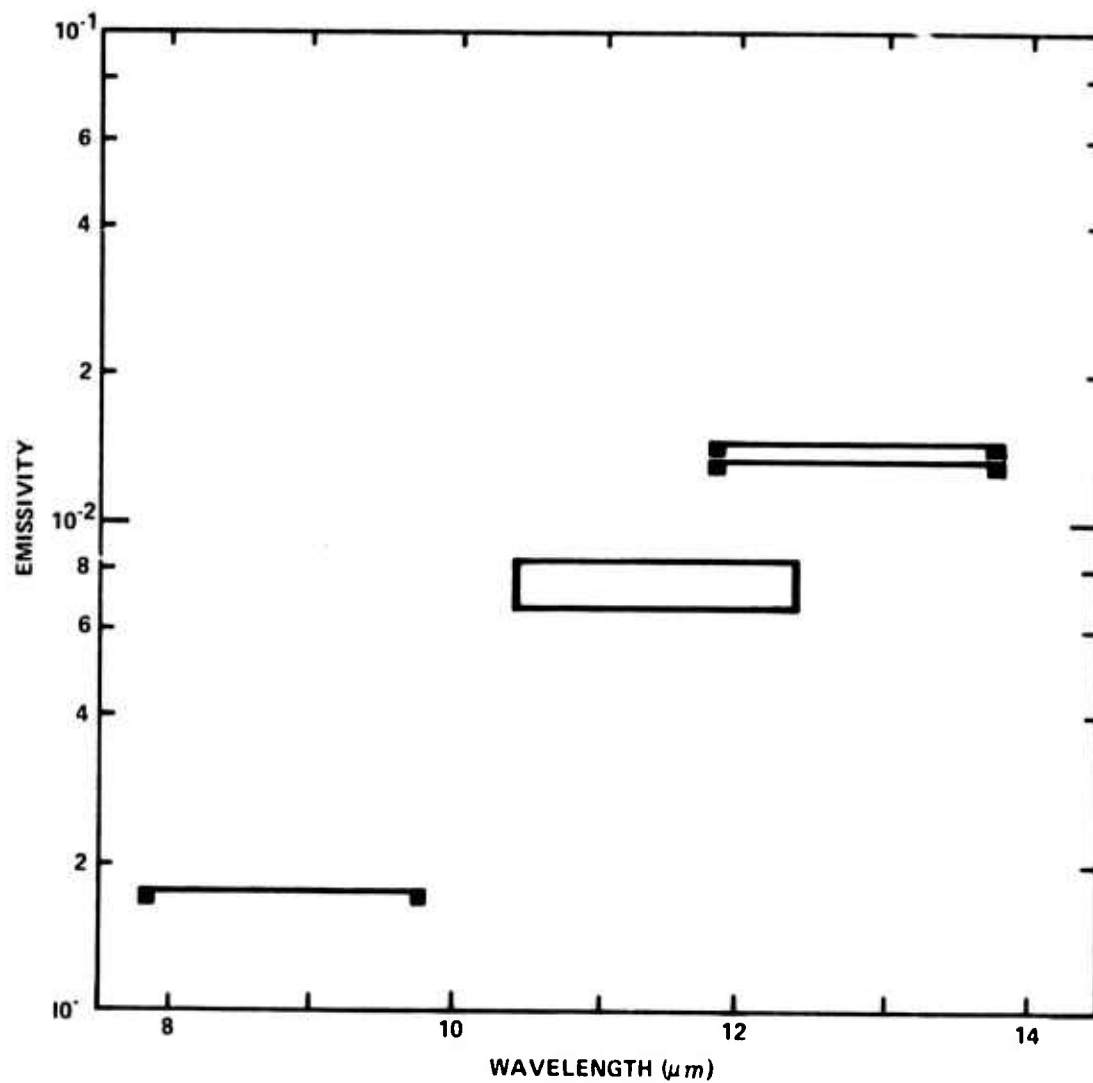


Figure 6. WAVELENGTH DEPENDENCE OF THE MEASURED EMISSIVITY FOR THE OXIDES OF URANIUM IN 5% OXYGEN/95% ARGON, AT $T = 4500^{\circ}K$. (U)

less than 10^{-5} of the original uranium remains as an atom or ion, the rest being combined in UO , UO^+ , UO_2 , UO_2^+ , and UO_3 . Finally, the various uranium oxides UO_x were summed, treated as one radiating species, and an integrated absorption coefficient deduced. The value obtained was approximately $3000 \text{ atm}^{-1} \text{ cm}^{-2}$.

3.2 LATER RESULTS

A series of experiments was undertaken in which the shock strength was increased in order to achieve higher test gas temperatures. Several features of the early data were found to change, which prompted further study of the system. One feature was the evidence of a rise of radiance from the gas toward the end of the normal shock tube test time, and which subsequently persisted some milliseconds well into the experiment. At these late times, driver and test gases are intermixed and cooled in the test chamber. Tests without aerosol addition also yielded persistent radiation. It was concluded that this radiation arose from rotationally excited water molecules resulting from the oxygen in the test gas reacting with the hydrogen driver gas. Tests using helium for a driver gas confirmed this conjecture. All subsequent tests were made with helium, as were the tests for the data of Figure 6.

But the tests at higher temperatures also showed the evidence of non-equilibrium test conditions in the test chamber. An example is shown in Figure 7, in which the radiance level does not achieve a steady plateau value, but decreases steadily during the test time interval. For these test conditions, it is known that the gas temperature rises very quickly to a constant value throughout the test time (the small amount of O_2 and uranium does not affect the overall gasdynamics). Thus, the record of Figure 7 indicates a kinetic process affecting the partial pressure of the LWIR radiating species.

One possible explanation is that the radiation results from shock heated aerosol particles, and the intensity decay reflects the particle vaporization time. This would imply that earlier data taken at the lower temperature of 4500°K was also mainly from particulates rather than uranium oxide molecules. However, estimates of particle vaporization times based on earlier measurements with other metals indicate that this is unlikely.

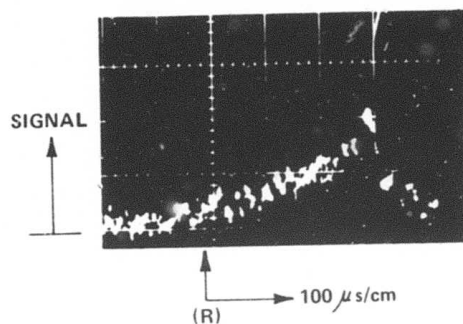


Figure 7. TIME DEPENDENCE OF 10-12 μm GAS RADIANCE AFTER SHOCK REFLECTION (R) FOR URANIUM AEROSOL IN 5% OXYGEN/95% ARGON AT 5400°K

In addition, the wavelength dependence of the measured emissivity does not exhibit the grey behavior that might be expected from continuum radiation from particulates.

The record of Figure 7 also resembles that of the typical "overshoot" seen in studies in which molecular dissociation behind shock waves is measured.⁵ Such a model would imply that some higher uranium oxide particle is rapidly formed in an excited state during the aerosol evaporation process and subsequently dissociates to an equilibrium partial pressure. This partial pressure would decrease with increasing temperature.

The funding and scheduling of the program did not permit a resolution of this nonequilibrium aspect of the late data. However, quite independent of the cause of this feature, the implication of the results indicate that the radiance levels unambiguously assignable to the uranium-oxygen system lie below the threshold of the present optical system. As such, only an upper limit to the band intensity is calculable, and a definitive value will require a more sensitive radiometer system.

The overall conclusions from the research to date and recommendations for the completion of the study of LWIR radiance from relevant metal oxides are presented in Section 6 of this report.

SECTION 4

(U) SUPPORTING EXPERIMENTS

4.1 SPECIES CONCENTRATIONS

As was discussed in previous sections, one of the principal advantages of using a shock tube to heat gases for spectrometric studies lies in the fact that the effects of shock wave processing are generally calculable. For gases in equilibrium behind incident and reflected shocks the final pressure and temperatures and species concentrations can be obtained in straightforward fashion. The necessary inputs are the initial conditions of pressure, temperature and gas constituency and the experimentally determined shock wave speed. Incorporation of the thermochemical properties of the gases then permit the calculations to be made. This procedure has been widely used and accepted for many years and has contributed significantly to the overall knowledge of the spectroscopic properties of gases.^{5,6}

The use of an evaporating metallic aerosol to produce samples for quantitative measurements is not equally straightforward. The principal complication arises from the unknown concentration of the resulting metal and metal-oxide species.

Under the program, a number of ways were considered to address this question. In general the methods involve either the measurement of the aerosol concentration itself in the shock tube prior to shock wave excitation, or the measurement of relevant gaseous species simultaneously with the recording of primary data.

Aerosol settling and sampling, radioactive counting and sample volume extraction techniques were considered. For work which requires less stringent reproducibility criteria, light scattering techniques are probably the most attractive for the measurement of aerosol distribution and concentration in the tube just prior to the test. Such measurements were made in previous programs involving aluminum aerosols. However, for quantitative work the particle size distribution must be known, and experience has shown that this parameter is influenced by initial conditions in the aerosol generating chamber, the discharge circuit parameters, and the

shock tube loading procedure. Because of the broad range of test conditions anticipated for this study, it was decided to pursue the question of species concentrations by direct measurements on selected species in the shock-heated gas sample under study.

Previous studies on the Al/O_2 system utilized the measurement of atomic Al line intensities, which, coupled with known transition probabilities permitted the atomic Al concentration to be established. Thermochemical properties of the Al/O_2 system were then used to deduce oxide concentrations, from which the radiance had been measured.

For the U/O_2 system more lines of varying strengths are available to make similar measurements; use of this redundancy can be made to establish the U atom concentrations with confidence. The chief limitation to this approach lies in the imprecision with which the thermochemical properties of the U/O_2 system are known. This particular issue is discussed in Section 5 and Appendix 1 of this report.

An example of the U line spectrum in the visible is shown in Figure 8. The prominent U line at 5915 \AA as well as many other lines of U and U^+ are well-developed and amenable to measurement. However, in the case of resonance lines, the question of the effects of optical thickness must be considered. Because of inherent unknowns for the requisite analyses, it was decided to attempt the direct measurement of the curves-of-growth for atomic lines in shock-heated samples with known U concentrations.

It was planned to use shock-heated UF_6 to produce U and/or U^+ lines over a range of concentrations and temperatures. Curves of growth of suitable lines from a heated, completely equilibrated sample of UF_6 would permit the quantitative assessment of U in the subsequent experiments with the aerosol. Use of UF_6 directly to obtain LWIR radiance is precluded because of the complications and contamination of the spectra. For spectra in the visible, any interference could be photographed and avoided. This does not apply to the inherently lower-resolution and non-photographable



Figure 8. EMISSION LINE SPECTRUM OF URANIUM AEROSOL IN ARGON AT 5700°K
(VISIBLE SPECTRAL REGION)

LWIR. Indeed, as has been demonstrated, the chief advantage of the pure-metal aerosol technique lies in the purity of the resultant spectra.

The experience with UF_6 proved unsuccessful on several counts. Primarily, no atomic lines were ever obtained in any of the spectra. An extensive number of shock tube experiments were conducted over a range of temperatures from 4500 to 9500°K, and with UF_6/A concentrations of 1 and 2%. The wavelengths of the photographed spectra extended from 2400-8000Å. Only a smooth continuum was recorded. It begins at 2500-2700Å and extends into the infrared. Further tests or attempts at the identifications of the continuum were abandoned, since the objectives of the UF_6 tests were not to be met.

Use of this fluorine compound proved to be quite injurious to the overall apparatus. Some of the tubing in the aerosol loading system had to be replaced; the heat transfer gauges, used successfully for shock wave velocity measurements for years without replacement, were chemically attacked and rendered inoperative; in addition, the shock tube windows were discolored and required repolishing.

An alternate technique for concentration measurements using atomic lines makes use of absorption spectra, where optically thin lines are known to be independent of line shape. The application of this technique to shock tube studies is illustrated by its use in molecular oxygen transition probability studies documented in Reference 7.

A short set of tests to demonstrate applicability to the U system was conducted with the apparatus shown schematically in Figure 9. Although the components of the system were not optimized for these tests, the results indicated that this technique would be of direct applicability to U line studies. The system uses a synchronized flash lamp as a bright source of visible continuum irradiance, which passes through the optical train consisting of the shock tube, a shutter and the spectrometer. As depicted in the figure, the object is to obtain an exposure on the plate which results primarily from the flash; the radiance from the gas is suppressed below plate response threshold by high flash intensity and a synchronized shutter. For the

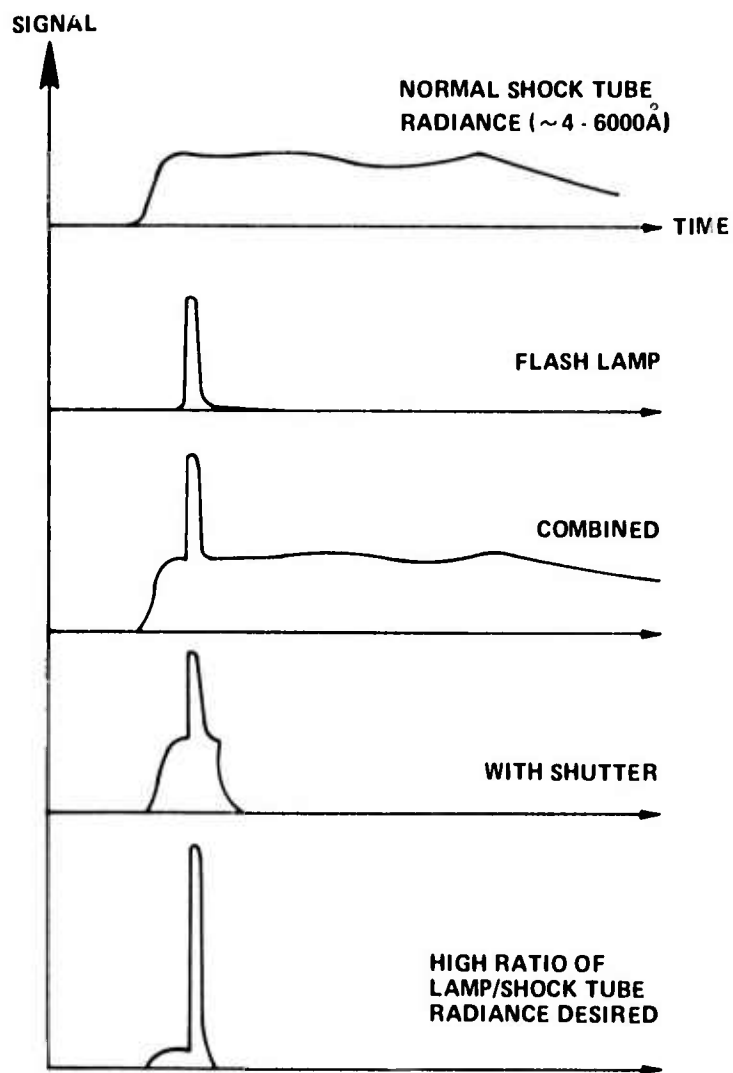
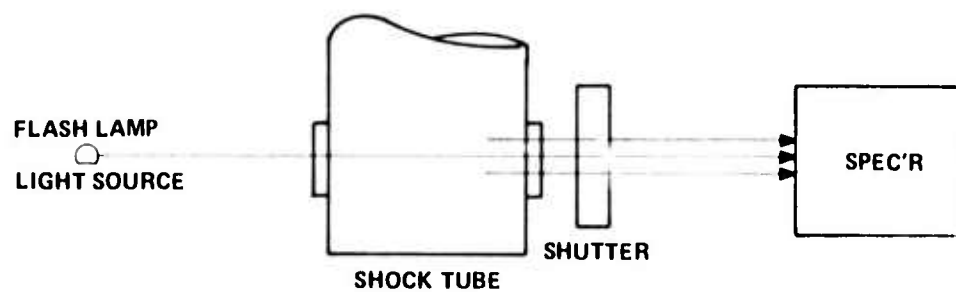


Figure 9. SCHEMATIC DIAGRAM OF THE OPTICAL TECHNIQUE FOR OBTAINING ABSORPTION SPECTRA OF SHOCK-HEATED AEROSOLS (SEE TEXT)

feasibility tests conducted, the available flashlamp was of marginally useful brightness. However, in the absorption spectrum, the sodium D lines were well developed, and the U line at 5915 Å was very faintly observed.

As a result of these tests, it is recommended that this technique is applicable to U-atom concentration measurements, made simultaneously with the recording of the primary LWIR radiance data.

A typical experimental setup for such measurements is discussed in Section 6.

4.2 AEROSOL GENERATION AND SPATIAL DISTRIBUTION

The metallic aerosols used to introduce metals in uniform suspension in the test gas are generated by exploding a suitable wire of the pure metal in a small chamber. The properties of such aerosols were extensively studied and reported in Reference 8. For example, the dependence of the particulate size distributions on discharge voltage was shown, and electron microscope photographs of several metals were demonstrated. In early work on aluminum aerosols in the Calspan experiments, the aerosols were carefully compared with those of Reference 8, from which it was concluded that identical results were being obtained.

Work with uranium showed that the capacitor discharge characteristics and the size of the wire were critical for reproducible results. Using a constant value of $C = 50 \mu\text{f}$ a variation of charging potential from 9 KV to 7.5 KV was seen to affect the aerosol properties, as measured by the resultant shock tube radiance. In addition, increasing the length of the wire from 13 to 25 mm produced similar changes. It was concluded that lowering the electrical energy per unit mass of U increased the aerosol particle size, which in turn affects the vaporization time behind the shock wave. Final experiments were all performed at high energies and short wires, for which the particulate sizes were all below $0.5 \mu\text{m}$ radius.

Consideration was also given to the spatial distribution of the aerosol in the shock tube after admitting the aerosol-laden test gas into the tube from the small generating chamber (Figure 1). Although not crucial to

the results, a uniform distribution is desirable. In early work with aluminum, laser scattering techniques were used to measure both distribution and particulate settling rates (from which size distributions could be confirmed). However, the technique illustrated in Figure 1 was found to be simpler, and used exclusively in subsequent tests. Radiance from the aerosol behind the incident shock wave is recorded at four window stations for each test. Independent of the processes or reactions taking place in the gas as it sweeps past each window, the height of the leading edge of the radiance pulse must be proportional to the amount of aerosol at that window station. The aerosol distribution can thus be readily monitored.

In general, it was found that the normal distribution is one which decreases monotonically toward the reflecting end of the shock tube. Further, it was found that the distribution could be modified by subsequent expansion or compression of the gas in the shock tube. Thus, the addition of a dummy volume at the end of the tank (subsequently valved off for the tests) resulted in a more uniform distribution over the central section of the shock tube. Reference to Figure 2 shows this section to be most relevant to reflected shock testing.

Results with this technique are shown in Figure 10. Record (A) for aluminum shows very satisfactory pulse heights and an ideal, uniform radiance level behind the incident shock wave. Incidentally, the growth of the test gas "slug length" as the wave progresses down the tube can also be readily seen. Such records were used to confirm predictions of shock tube performance in terms of the distance-time graphs such as shown in Figure 2.

Similarly ideal results with uranium aerosols were more difficult to achieve, although the final distribution was considered satisfactory, as indicated in Figure 10(B).

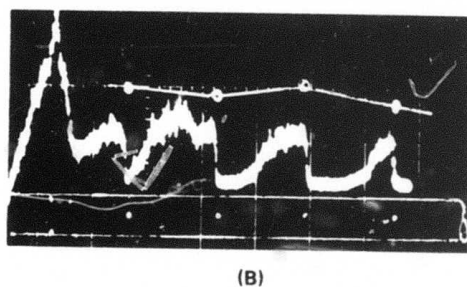
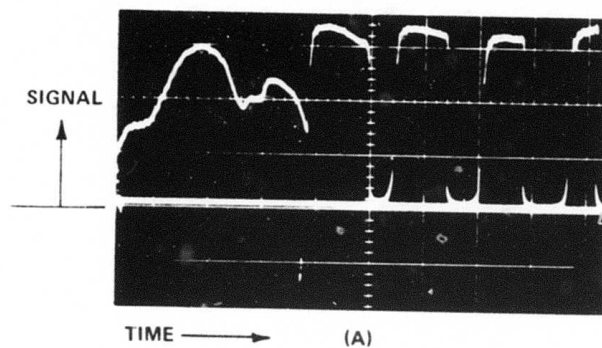


Figure 10. TYPICAL RECORDS OF GAS RADIANCE BEHIND THE INCIDENT SHOCK DURING PASSAGE DOWN THE SHOCK TUBE. THE HEIGHT OF THE LEADING EDGE OF THE PULSE IS PROPORTIONAL TO THE AEROSOL CONCENTRATION AT THAT STATION. (A) ALUMINUM, (B) URANIUM. SWEEP RATE WAS 500 $\mu\text{s}/\text{cm}$.

SECTION 5

SUPPORTING THEORETICAL CONSIDERATIONS

Calculations have been performed to determine the equilibrium composition of the shock-heated uranium-oxygen-argon mixture over a range of temperatures and partial pressures of the constituents. The solution of the equilibrium equations is obtained very quickly with an existing IBM program, once the thermodynamic properties of each of the product species has been determined. An accurate evaluation of these thermodynamic functions at high temperature is required for an accurate equilibrium solution, and involves extrapolation of available data from 2500°K to 8000°K.

The species that have been considered as constituents of the shock-heated gas are U, U^+ , O, O^+ , UO , UO^+ , UO_2 , UO_2^+ , UO_3 , Ar, Ar^+ , and e^- . (The argon chemistry is coupled to the problem only through the electron concentration.) Partition functions for O_2 , O^+ , Ar and Ar^+ were available. For preliminary calculations, simple extrapolations of available data⁹ for other species were used. More detailed calculations were available for final comparisons with experiment. The preliminary extrapolations are based on the enthalpy and free enthalpy functions given in Reference 9 and the ionization energies given in Reference 10. They assume a classical, fully excited model for each of the species.

The preliminary calculations were performed for three different concentrations of uranium vapor and for four combinations of argon/oxygen concentrations. The temperature range covered was from 3000°K to 8500°K. A typical variation with temperature is shown in Figure 11. It can be seen that at relatively low temperatures most of the uranium is combined into oxides. This is consistent with the experimental finding that the uranium line spectrum disappears when a small amount of oxygen is added to a uranium-argon mixture in the shock tube. At temperatures of 7000°K and higher, the atoms (U and U^+) are in higher concentration than the oxides and the atomic spectra should reappear at these higher temperatures. When the oxygen concentration is increased by a factor of ten, the oxide outnumbers the atoms by a factor of 100 at 7000°K. Thus, it is clear that a careful evaluation of the thermodynamic properties of the species was necessary for final reduction of the spectroscopic data (Appendix I).

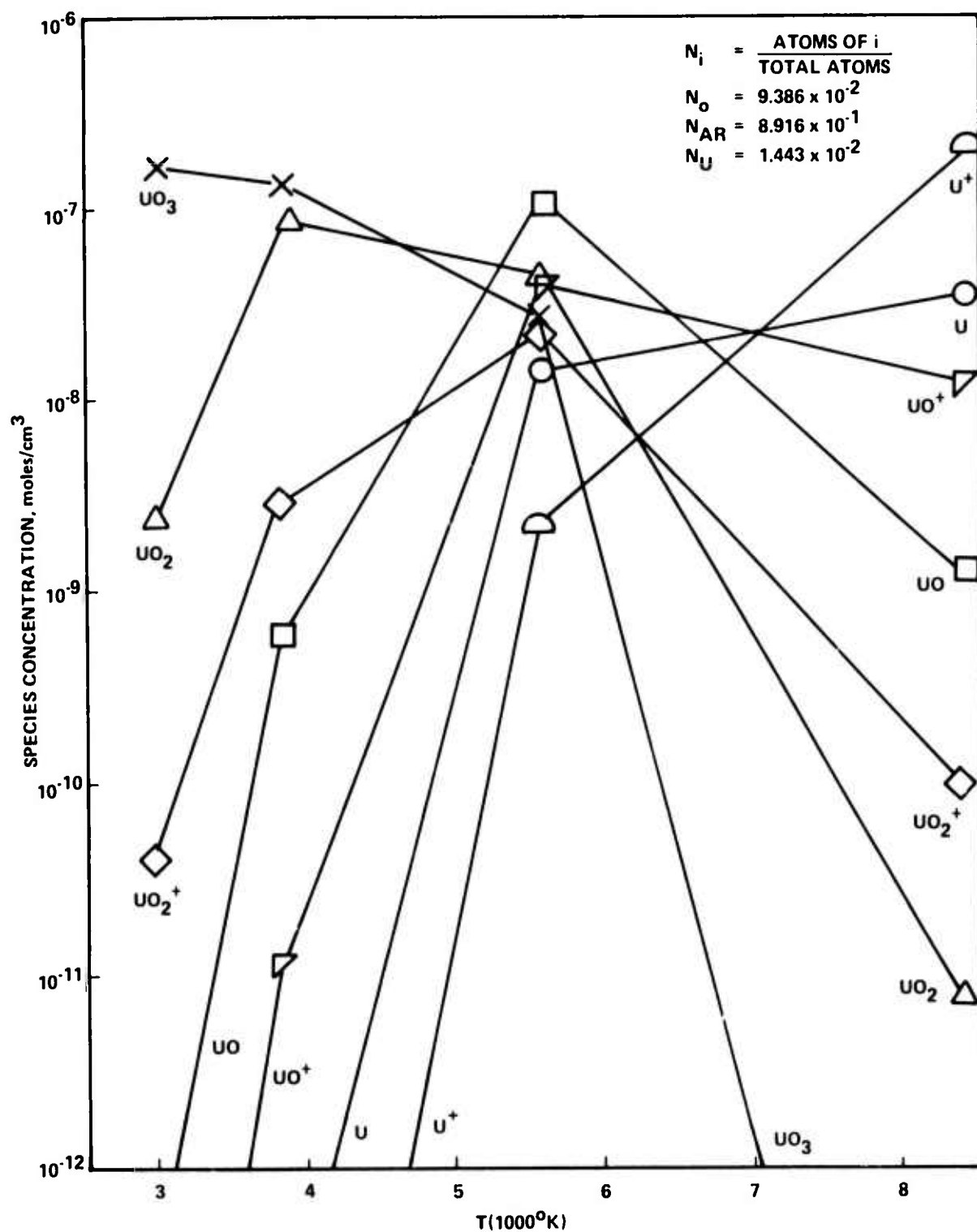


Figure 11. CALCULATED SPECIES CONCENTRATIONS FOR GIVEN CONDITIONS

For the more detailed calculations, the best available knowledge of the energy levels of the species were utilized.¹¹ For U and U⁺, energy levels are tabulated up to about 10,000 cm⁻¹. The usual relation for the partition function,

$$Q = \sum_{i=0}^{\infty} g_i e^{\frac{-E_i}{kT}}$$

was divided into two terms, so that

$$Q = \sum_{i=0}^{n-1} g_i e^{\frac{-E_i}{kT}} + \bar{g} \left(\frac{\eta}{\Delta E} \right) kT e^{\frac{-E_n}{kT}}$$

The first term is a sum over the n known levels, and the second term is an integral over the remaining higher energy terms. $\left(\frac{\eta}{\Delta E} \right)$ is the average density of levels and \bar{g} the average degeneracy, so that $\bar{g} \left(\frac{\eta}{\Delta E} \right)$ is the average density of states, and is assumed constant. The lower energy states are not classified, so their individual degeneracies are not known. This has led to the further simplification that all the lower states are taken to have the same degeneracy, also taken as \bar{g} . Thus the final formulas used for U and U⁺ are

$$\frac{Q}{\bar{g}} = \sum_{i=0}^{n-1} e^{\frac{-E_i}{kT}} + \left(\frac{\eta}{\Delta E} \right) kT e^{\frac{-E_n}{kT}}$$

and the internal energy is given, within the same approximation, as

$$\frac{E}{kT} = \frac{\frac{1}{kT} \sum_{i=0}^{n-1} E_i e^{\frac{-E_i}{kT}} + \left(\frac{\eta}{\Delta E} \right) [E_n + kT] e^{\frac{-E_n}{kT}}}{\sum_{i=0}^{n-1} e^{\frac{-E_i}{kT}} + \left(\frac{\eta}{\Delta E} \right) kT e^{\frac{-E_n}{kT}}}$$

The average density of energy levels, $\left(\frac{\eta}{\Delta E} \right)$, was taken equal to 2×10^{-3} cm for both U and U⁺, consistent with the value for the known levels. For U, $n = 2$, $E_{n-1} = 13,463$ cm⁻¹. For U⁺, $n = 16$, $E_{n-1} = 8394$ cm⁻¹. The results of these calculations agree within a few percent up to 2500° K, with those of Reference 9 for uranium atoms.

Additional considerations of uranium and uranium-oxide thermo-functions are presented in Appendix I.

SECTION 6

CONCLUSIONS AND RECOMMENDATIONS

As discussed in Section 3, the preliminary estimate of an overall engineering band strength for the $\text{U}-\text{O}_2$ system yielded a value of $3000 \text{ cm}^{-2} \text{ atm}^{-1}$, for measurements made at 4500°K . Subsequent tests at 5400°K raised the question of the attainment of complete equilibrium; pending the resolution of this point, the results to date provide an upper level for the band strength of $500 \text{ cm}^{-2} \text{ atm}^{-1}$. This value was derived by scaling the early results to the minimum intensity discernable with the present detecting system.

The limiting performance of the LWIR system depicted in Figure 1 corresponds to one with an effective background temperature of about 350°K . This is taken to mean that blackbody radiance at that temperature produces a signal equal to overall system noise.

The improvement in performance needed to meet and definitively resolve the objectives of the program can be achieved by the use of a different detector/optics system. A Ge:Hg detector with liquid nitrogen cooled optics is recommended. A schematic diagram of such a system is shown in Figure 12. The entire test section, including the windows and light trap are at LN_2 temperature, so that the detector sees essentially a surrounding environment near 80°K . Care in baffling for reflective stray light rejection must be exercised. The system shown also incorporates the absorption spectrum recording system for the simultaneous measurement of atomic line strengths for species concentration determinations.

The improvement in radiance threshold that accrues from such a system can be assessed by examining the relevant blackbody temperature dependence shown in Figure 13. At $10 \mu\text{m}$, lowering the effective background temperature even to 135°K yields an improvement of 1000 X. This is an overconservative estimate; in LWIR scanning spectrometers recently implemented at Calspan in which much more difficult design constraints were imposed, effective backgrounds of 120°K were achieved.

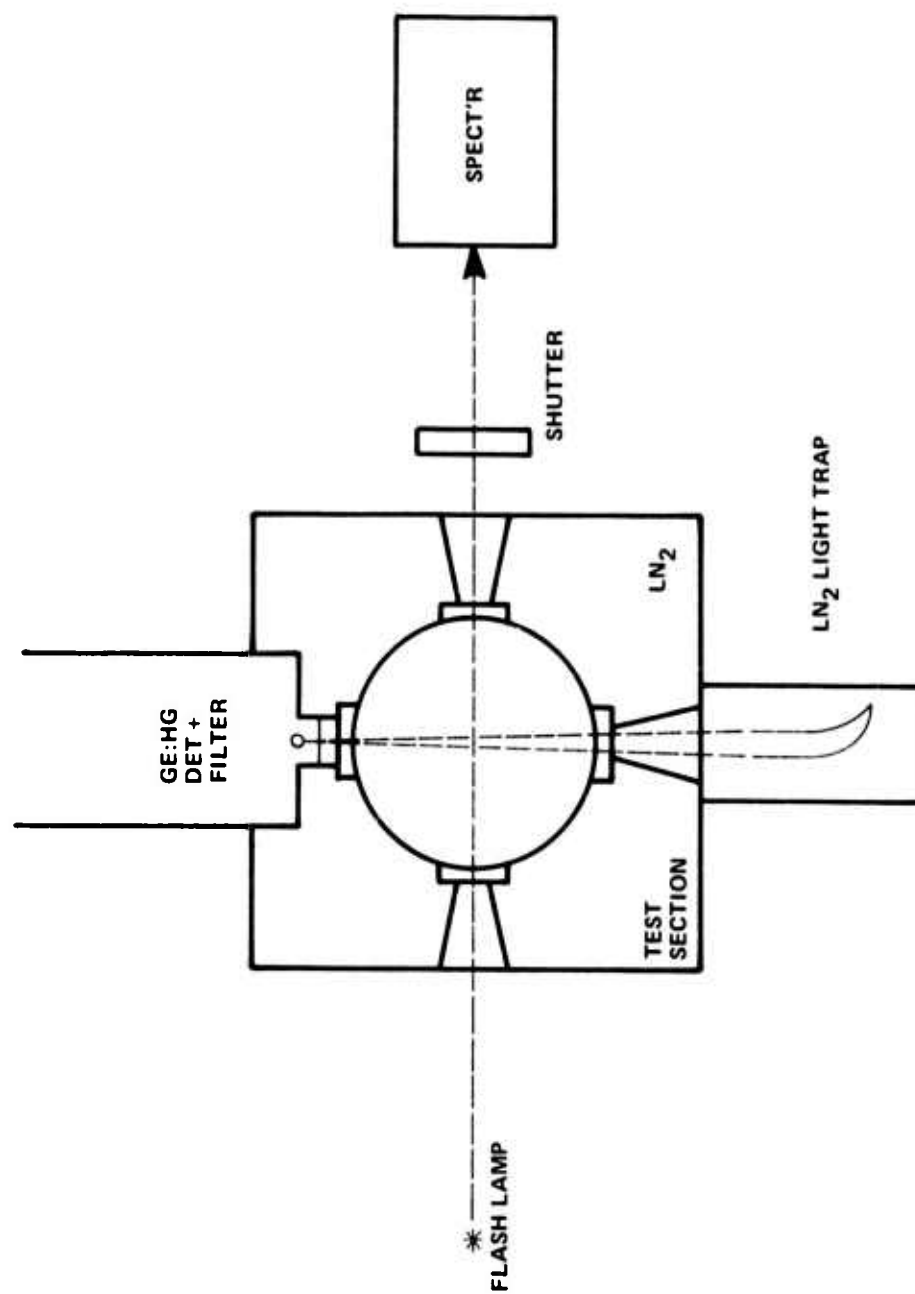


Figure 12. APPARATUS FOR SIMULTANEOUS ATOMIC ABSORPTION AND HIGH-SENSITIVITY LWIR RADIANCE MEASUREMENT

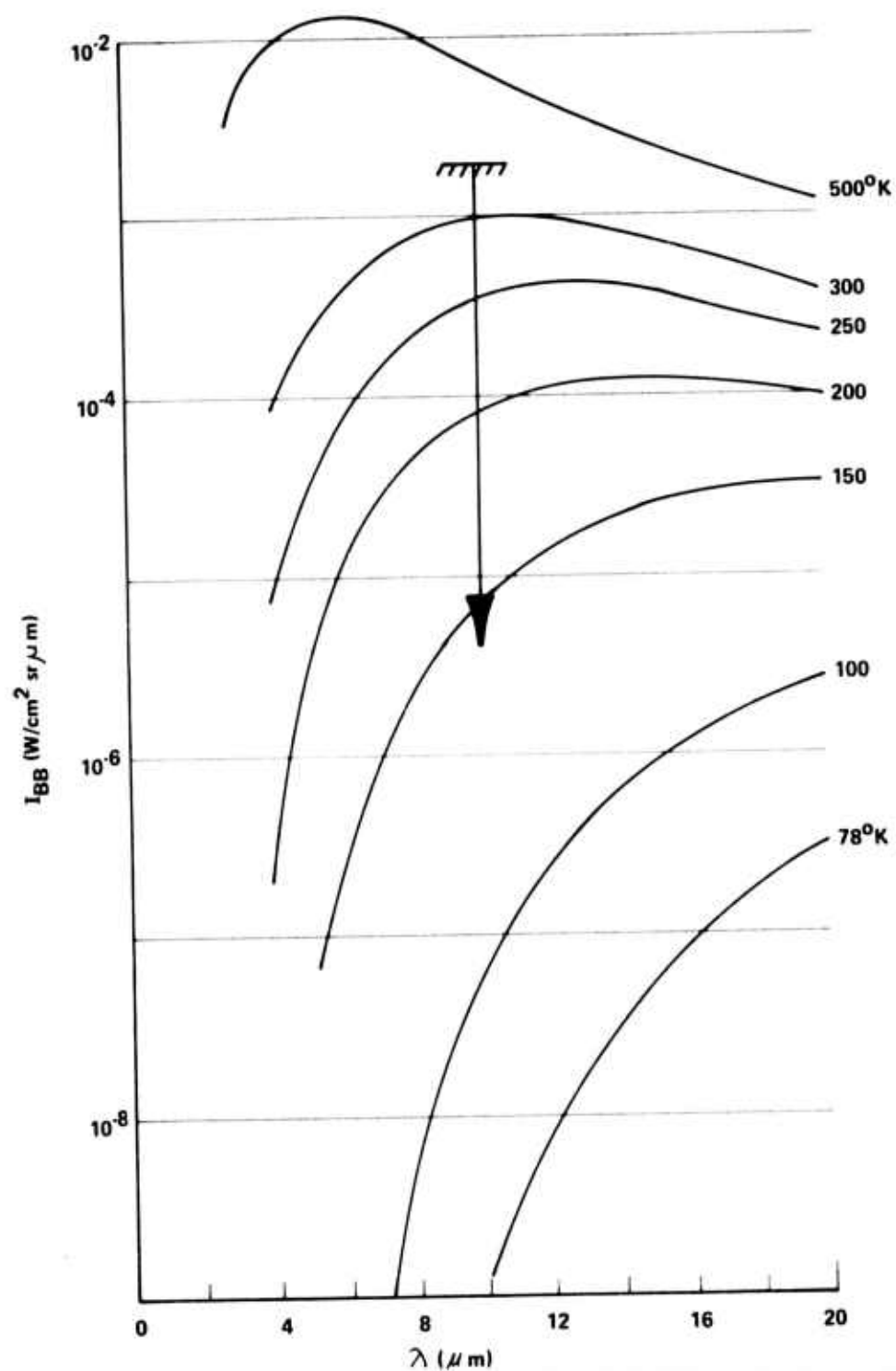


Figure 13. BLACKBODY RADIANCE CURVES SHOWING THE EFFECT OF DECREASING THE BACKGROUND TEMPERATURE FROM 350 °K

Such improvements can be traded off in a number of ways in terms of LWIR radiance measurements from metal oxides. Not only can the requirements for concentration levels of relevant species be reduced, but spectral resolution can also be improved. Thus, measurements can be extended to higher temperatures which remove the question of the attainment of equilibrium test conditions; and even at the lower resultant oxide concentrations, LWIR radiance measurements with higher resolution ($\sim 0.5 \mu\text{m}$) can be made.

REFERENCES

1. R. W. Nicholls, W. H. Parkinson, and E. M. Reeves, *Appl. Optics*, 2, 919 (1963)
2. R. Watson, A. L. Morsell, and W. J. Hooker, *Rev. Sci. Instr.*, 38, 1052 (1967)
3. T. J. Falk, *J. Chem. Phys.*, 48, 3305 (1968)
4. W. H. Wurster, *Phys. Fluids Suppl. I*, I-92 (1969)
5. *The Shock Tube in High-Temperature Chemical Physics*, Gaydon, A. G. and Hurle, I. R., Rheinhold Publishing Corporation, New York, 1963.
6. W. H. Wurster, *J. Quant. Spectrosc. Rad. Transfer* 3, 355 (1963).
7. C. E. Treanor and W. H. Wurster, *J. Chem. Phys.*, 32, 758, 1960.
8. F. G. Kariotis, B. R. Fish and G. W. Royster, Jr., *Aerosols from Exploding Wires*, pg. 299 in *Exploding Wires*, Vol. 2, edited by W. Chase and H. Moore, Plenum Press, New York, 1962.
9. A. Pattoret, J. Drowart and S. Smoes, *Thermodynamics of Nuclear Materials 1967*, Int. At. En. Agency, Vienna (1968).
10. J. B. Mann, *J. Chem. Phys.*, 40, 1632 (1964).
11. *Experimental Transition Probabilities for Spectral Lines of Seventy Elements*, NBS Monograph 53, 1962, by C. H. Corliss and W. R. Bozman.
12. *JANAF Thermochemical Tables*, The Dow Chemical Company, Midland, Michigan, August 1965 and updates.
13. "Statistical Mechanics", Mayer, J. E. and Mayer, M. G., John Wiley and Sons, Inc., New York, 1959. The JANAF Tables follow this reference in the formulations of the various thermodynamic functions and the higher order corrections to the vibration-rotation partition functions.

14. D. W. Steinhaus, L. J. Radziemski, Jr., R. D. Cowan, J. Blaise, G. Guelachvili, Z. Ben Osman and J. Verges, Los Alamos Scientific Laboratory, Report No. 4501, October 1971.
15. S. Abramowitz, N. Acquista and K. R. Thompson, J. Phys. Chem. 75, 2233 (1971).
16. S. D. Gabelnick, G. T. Reedy and M. G. Chasanov, Chem. Phys. Lett. 19, 90 (1973).
17. H. H. Michels, Private Communication, 1972.
18. H. L. Schick, "Thermodynamics of Certain Refractory Compounds", Academic Press, 1966.
19. M. Kaufman, J. Muentner and W. Klemperer, J. Chem. Phys. 47, 3365 (1967).
20. J. Muentner, Private Communication. The possibility that the observed polarity of UO_2 was owing to a vibrationally induced moment in a linear UO_2 was ruled out.
21. G. De Maria, R. O. Burns, J. Drowart and M. G. Inghram, J. Chem. Phys. 32, 1373 (1960).

APPENDIX I
NOTES ON URANIUM AND URANIUM OXIDE THERMO FUNCTIONS
John Raymond

Thermodynamic functions have been computed for the following species all as ideal vapors: U(I), U(II), UO, UO^+ , UO_2 , UO_2^+ , UO_3 , UO_3^+ . Values of $(F^\circ - H^\circ_0)/T$, $(H^\circ - H^\circ_0)/T$ and $H^\circ - H^\circ_0$ in units of cal-mole⁻¹-deg K⁻¹ and kcal/mole have been tabulated. The reference state temperature is 298°K, for consistency with the JANAF Tables.¹⁴ The temperature range covered in these calculations is 2000-8000°K in 500° intervals. The theoretical formulation starts from the partition functions and is well known.¹³ The main effort consisted of enumerating the available energy states of the various species. Experimental data were used where available, but since little reliable data could be found, some extrapolations based upon chemical reasoning were also involved. The procedure used to evaluate the partition function for each species are summarized below.

U(I) AND U(II)

Relatively new spectroscopic data and assignments are now available for these species.¹⁴ 904 states with energies up to about 38000 cm⁻¹ for U(I) and 273 states with energies up to 45000 cm⁻¹ for U(II) have been assigned, at least with regard to the J value. The partition functions for U(I) and U(II) were summed directly over these energy states using a simple computer code. For U(I) at 8000°K the total internal partition function Q_{INT} computed is 204.9093 and the highest energy state contributes 0.0180. For U(II) at 8000°K, $Q_{\text{INT}} = 155.8241$ and the highest state contributes just 0.0036. No correction for omitted higher states was attempted.

UO, UO^+

Spectroscopic information on UO is scarce and for UO^+ is nonexistent. Matrix IR work by Abramowitz et al.¹⁵ and by Gabelnick et al.¹⁶ has led to conflicting values for the IR fundamental of UO. The work by Gabelnick et al. was at higher resolution and included careful study of spectra as a function of the temperature and composition of the condensed uranium oxide. In consequence, their results were used in preference to those of the former authors. They give a fundamental for UO, as well as

symmetric and asymmetric stretches for UO_2 and the two stretching frequencies of UO_3 , but no other spectroscopic constants for UO could be deduced from their data.

However, H. H. Michels is presently analyzing quantum mechanical calculations he has done on UO and UO^+ .¹⁷ He obtains potential curves and spectroscopic constants for the ground and several excited states of UO and UO^+ . The calculations are very complex due to the large number of electrons which must be considered and especially because of the involved angular momentum couplings that result from the f^3ds^2 and f^3s^2 configurations of U and U^+ respectively. The ground state of UO is predicted to be $^7\pi$ and that of UO^+ should be $^4\pi$. Each species has a host of low lying excited states of symmetries $^7\pi$, $^7\Delta$, $^7\Sigma^\pm$, $^5\pi$ and $^5\Delta$ for UO and $^4\pi$, $^4\Delta$, $^4\Sigma^\pm$, $^2\pi$, $^2\Delta$, $^2\Sigma^\pm$ and $^2\phi$ for UO^+ and only a portion of these have been analyzed in any detail yet. The results of the analysis were used as received in the thermodynamic calculations.

One major result is that the electron lost in making UO^+ from UO has little effect on bonding, and very similar spectroscopic constants are predicted for UO , UO^+ and their low lying excited states. Therefore the same set of spectroscopic constants was adopted for both UO and UO^+ for calculating the vibration-rotation part of the partition. Anharmonicity corrections calculated as given in Mayer and Mayer¹³ were included. For the electronic part of the partition functions summations were extended just over the states which had been analyzed by Michels and for which energies and degeneracies were given. The excited electronic states were assumed to have the same vibration-rotation spectrum as the ground states. This is a reasonable assumption due to the non-bonding nature of the f and d electrons, which electrons give rise to the low lying excited states. No attempt was made to estimate corrections for omitted electronic states since insufficient information is available for estimating excited state densities.

UO_2 , UO_2^+

Because a non-bonding electron is probably lost in forming UO_2^+ from UO_2 , these two species were assumed to have identical geometries and spectroscopic constants. Thus, they have identical vibration-rotation partition functions. The stretching frequencies of Gabelnick et al.¹⁶ were

used while the bending frequency was estimated by comparison with bending frequencies given for CrO_2 , MoO_2 , and WO_2 (which are valence isoelectronic with UO_2) by Schick.¹⁸ Although Gabelnick deduces that UO_2 is linear on the basis of a valence force model and using isotopic vibration frequency data, the molecular beam electric deflection experiments of Kaufman et al.^{19, 20} strongly suggest that UO_2 is bent. The bond angle was assumed to be 107° and the bond lengths were chosen equal to the UO bond length given by Michels' calculation.¹⁷ An anharmonicity correction equal to 3 times (for the 3 modes of bending) that for UO was included in the partition function.

No definitive experiments or calculations on the electronic spectrum of UO_2 have been done. Therefore, electronic contributions for UO_2 and UO_2^+ equal to those calculated from Michels'¹⁷ calculations were taken for UO and UO^+ respectively.

UO_3 , UO_3^+

The same procedures used for UO_2 and UO_2^+ were used. Gabelnick's stretching frequencies were used and the bending frequencies were estimated by comparison with CrO_3 , MoO_3 and WO_3 again using data given by Schick.¹⁸ A planar symmetric geometry was assumed with the bond lengths equal to the UO bond length. Identical ground state partition functions were assumed for UO_3 and UO_3^+ , while the electronic contributions were again taken equal to those for UO and UO^+ . Anharmonicity corrections equal to 6 times that for UO (because there are 6 normal modes) were added.

Discussion

Considerable uncertainties are still involved. The thermodynamic functions for U(I) and U(II) may be considered reliable, but little is known about any of the oxides. It is intended to update the UO and UO^+ calculations as more of Michels' calculated results become available. His calculations, though still relatively crude, predict such a confusing array of low-lying states that it is hard to see how definitive electronic spectroscopy will be done in the foreseeable future. The high chemical reactivity of all the uranium oxides at the temperatures needed to make vapors of them will also hinder attempts at definitive spectroscopy.

The procedure used for estimating the unknown frequencies of UO_2 and UO_3 is a reasonable one, but is still subject to errors, the most serious of which is that many of the frequencies of CrO_2 , MoO_2 , WO_2 , CrO_3 , MoO_3 and WO_3 were themselves estimated by Schick¹⁸ employing the admittedly crude valence force model together with empirical ratios between stretching and bending force constants.

There is one further difficulty with the UO_3 - UO_3^+ pair. The published ionization potential for UO_3 (~ 10 eV) is about 4 eV higher than those for U(I) , UO and UO_2 .²³ Either it is an incorrect value or the nature of the ionized electron is considerably different from those in UO and UO_2 . In particular, a 10 volt electron is likely to be rather bonding. Therefore, taking the same geometry and ground state spectroscopic constants for UO_3^+ as for UO_3 (guessed in the first place) is more questionable than is the corresponding procedure for UO , UO^+ , UO_2 and UO_2^+ .

In summary, it is felt that the thermodynamic functions calculated in this work for the uranium species of interest are the best relatively consistent set of values available and that further improvements in their accuracy must await new reliable spectroscopic data on the molecules.